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Hydrothermal Liquefaction: Path to Sustainable Aviation Fuel

November 17–19, 2020, Virtual Workshop in ZOOM Platform

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Summary

The virtual workshop to accelerate the commercialization of “hydrothermal liquefaction technology to produce sustainable aviation fuel” brought together a wide range of experts in hydrothermal liquefaction and sustainable aviation fuel, as well as renewable energy stakeholders across the globe, to discuss the current state of this process and identify short- and long-term research opportunities.

Workshop participants identified several priority activities. Some of these activities apply broadly to wet waste conversion via the hydrothermal liquefaction process, while others apply specifically to sustainable aviation fuel. Across these identified priority activities, the following four focus areas emerge.

1. **Feedstock Availability and Formatting**: Developing hydrothermal liquefaction technology that is amenable to a variety of waste feedstocks; understanding the mitigation strategy for feedstock variability; studying feedstock homogenization and rheology for pumping feedstocks at varying solid rates and blends to the reactor interface.
2. **Hydrothermal Liquefaction Process**: Development around the hydrothermal liquefaction reactor scale (large vs. modular); improving energy intensity and cost through process heat integration; optimizing biocrude recovery; optimizing biocrude yields through reactor design, feed selection and formatting, and catalytic methods; demonstrating hydrothermal liquefaction operation with a longer time on stream to de-risk scale-up.
3. **Upgrading and Refining**: Removal of minerals before biocrude upgrading; heteroatom removal during upgrading and especially hydrodenitrogenation for application of sustainable aviation fuel; demonstration of catalyst stability with longer time on stream; American Society for Testing and Materials (ASTM) specification for sustainable aviation fuel.
4. **Value Added**: Understanding value along the supply chains; identifying solutions for all the product streams (e.g., aqueous, solids, biocrude); measuring the value derived from pollution avoidance, social justice, and other economic services. The aqueous product and solids are currently liabilities but have potential as valuable co-products with a low-cost conversion or separation strategy.

Activities identified during the workshop as having the potential to accelerate the commercialization of sustainable aviation fuels via the hydrothermal liquefaction process from wet waste feedstocks are summarized in Figure ES. 1.

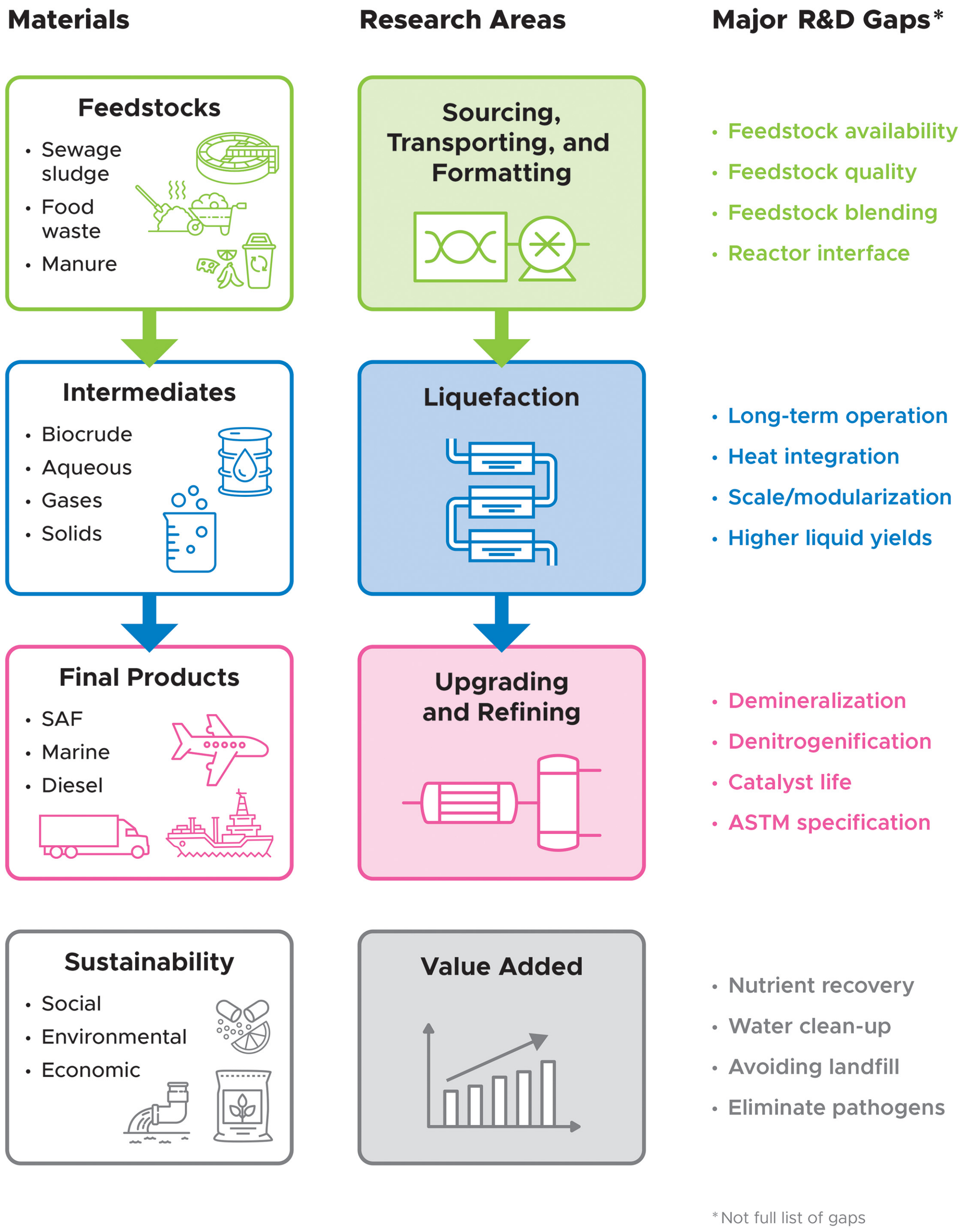

Figure ES. 1. Major research opportunities identified in commercializing hydrothermal liquefaction to sustainable aviation fuel.

Acknowledgments

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Acronyms and Abbreviations

ASTM	American Society of Testing and Materials
BETO	Bioenergy Technologies Office
CAAFI	Commercial Aviation Alternative Fuels Initiative
HTL	hydrothermal liquefaction
PNNL	Pacific Northwest National Laboratory
SAF	sustainable aviation fuel
TAN	total acid number
UV	ultraviolet
WRRF	water resource recovery facility
FOG	Fats, Oil and Grease

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1.0 Introduction

A variety of technologies are currently under development for producing sustainable aviation fuel (SAF), and one of the most promising technologies is the hydrothermal liquefaction (HTL) of low-cost waste feedstocks. Organizations across the globe are conducting research and development on HTL technology at scales varying from the laboratory to demonstrations focused on various aspects of technology development. The identification of more advanced and sustainable solutions to maximize the fuel yield while optimizing fuel properties and achieving cost parity with conventional fuels is the major focus in developing HTL technology.

This workshop on the application of HTL to produce SAF, coordinated by the U.S. Department of Energy Bioenergy Technologies Office, Commercial Aviation Alternative Fuels Initiative, and Pacific Northwest National Laboratory (PNNL), was held virtually on November 17–19, 2020. A broad spectrum of experts from industry, academia, national laboratories, and government from across the globe participated in the workshop, contributing their ideas, insights, and perspectives.

A series of keynote presentations, plenary presentations, and breakout sessions provided an interdisciplinary framework for sharing information and building collaboration. This document provides an overview of the content discussed in the presentations as well as the breakout session discussion. Diverse stakeholder perspectives were gathered, and this wealth of information collectively provides an update on the current state of the field and identifies the key research opportunities.

2.0 Product Quality

Turbine-powered aircraft are designed around reliably converting the chemical energy embodied in hydrocarbon fuels into thrust that powers the aircraft. The aircraft and engine are therefore certified to operate on a specific jet fuel specification. The fuel must remain a pumpable, inviscid liquid at very cold temperatures that allows an engine to restart in the event of engine blow out while also being safe for ground crews to handle. Aviation fuels, therefore, have tight specifications defined by the American Society of Testing and Materials D1655 (ASTM D1655).

Modern jet fuels consist of broad boiling point mixtures of normal-, iso-, and cycloalkanes as well as aromatics. The various hydrocarbon families impart different fuel properties. Specific energy (MJ/kg) is enhanced by the compositional fraction from the n- and iso-alkanes. Energy density (MJ/L) is enhanced by the compositional fraction of cycloalkanes and aromatics. The freeze point is enhanced by the presence of iso- and cyclo-alkanes and aromatics. Sooting is a major downside of having a high aromatics fraction. For this reason, the aromatic content should be maintained to the minimal amount required. For legacy reasons, aircraft may require some level of aromatics for seal swelling to prevent fuel line leaks. These four families of compounds are produced from HTL and upgrading of wet waste, such as sewage sludge, and food or woody material.

Just as important as the chemical families that make up jet fuel is understanding what chemical compounds must be limited to small quantities to assure fuel integrity and stability. Unsaturation (double bonds), heteroatoms (organic O, N, S), and metals (e.g., transition metals, alkali metals) need to be kept at very low amounts—less than 1%—and often at ppm levels to assure fuel integrity and stability.

The fuel specification and approval process is rigorous. ASTM D4054 defines the SAF evaluation and qualification process. ASTM D7566 documents the qualifying feedstock, conversion processes, and fuel properties and constraints in an annex. While the initial fuels qualified in ASTM D7566 were n- and iso-alkanes, Annex 6, which is based on a hydrothermal process that uses supercritical water to process fats, oils, and greases, was approved in 2020. As described above, SAF consists of all four hydrocarbon families, similar to what would be present from hydrothermal processes, either sub or supercritical, for the feedstocks covered in this report. The approval of Annex 6 is important because a fuel with similar composition to HTL process can facilitate approval for annexes that cover fuels using a similar process to make a comparable product, although from a different feedstock.

ASTM D4054, which is the standard practice covering the fuel evaluation and qualification process, was updated to include a “fast-track.” The fast-track option can be used, with ASTM D02.J subcommittee approval, when the SAF contains the same molecules that are in petroleum jet fuel (n- and iso-alkanes, cycloalkanes that are typical in petroleum, and aromatics), and this is the case for HTL. The fast-track process limits the SAF blend in jet fuel to 10%, but it does produce a qualified fuel faster and with less expense. (Note, the fuels qualified under ASTM D7056 Annexes 1–3, 5, and 6 allow a 50% blend of SAF in petroleum.) Annex 4 is for a single-component SAF (farnasane) and limits SAF content in the jet fuel to 10%. Finally, to aid researchers and provide initial indications of SAF quality, the University of Dayton is proving two early analysis “tiers” referred to as alpha and beta. Within these tiers, only small quantities of product are needed to gain an early indication of the fuel quality. Fuel evaluation and qualification will still be required, but the early analysis can provide indications on fuel property attributes that can be improved with additional process research and development.

2.1 Summary and Analysis

Aircraft and their engines are certified to fly only with a fuel that meets tight specifications. SAF from HTL using waste sources and classical biomass must be able to meet these specifications. HTL produces the four hydrocarbon families allowed in jet fuel—n-, iso-, and cycloalkanes, and aromatics. However, the fuel also contains small or trace quantities of N-containing heterocyclic compounds. Future research will need to address the removal of these species or add a polishing step to remove trace components. We will need to pay attention to other impurities in SAF from HTL as well. This focus on trace components has not been pursued because the trace components are not a concern with diesel fuel. The recent addition of a fast track for ASTM qualification and the approval of ASTM D7056 Annex 6 will aid and likely ease the cost of ASTM pathway approval. Further, more early testing is now possible through alpha and beta testing, which can provide researchers with early indications of the fuel quality in small samples. A better understanding of the role of hydrogenating aromatics is needed to produce cycloalkanes, especially regarding how much hydrogen is required. Additional information about the need for polishing hydrotreaters is also vital because the equilibrium between cycloalkanes and aromatics is affected by such.

2.2 Research Opportunities in Product Quality

- Heteroatom removal (N): the maximum combined heteroatom concentration allowed in aviation fuel is below 0.5%, but the specification for the N in jet fuel is not defined properly because the N levels in fossil-derived jet fuel are almost negligible. This limits the knowledge of the impact that N compounds have in aviation fuel and requires meeting similar N levels in the SAF to those in conventional jet fuel, which are less than 10 ppm. Given the high N levels in the wet waste-derived biocrude, catalyst and process development for N removal from the biocrude is critical.
- Maximizing jet fraction yield: the average jet fuel carbon number is ~11.4, and the carbon distribution falls primarily between 8 and 16. However, only 20–25% of the wet waste-derived biocrude typically falls in this range. Research on cracking the heavies to maximize the jet fraction yield from the biocrude will benefit the overall economics towards producing SAF from HTL process.
- Prescreening for SAF: early-stage participation in the two-tiered (Tier α requires 1–5 mL, and Tier β requires 15–500 mL) prescreening process for SAF will reduce the time and resources required to develop HTL-derived biocrude upgrading strategies to meet the ASTM qualifications.

3.0 Feedstock Matters and Formatting

3.1 Environmental Liability of Wet Wastes

Workshop participants noted that a key value proposition for HTL is its ability to reduce waste volumes at levels far beyond anaerobic digestion (90% vs. ~50%). In the United States, wastewater solids disposal costs exceed $3.3 billion annually (an average of $400/dry ton including all solids treatment and disposal related costs).[1] This represents a major operational cost to municipalities. These costs are increasing as organic waste disposal regulations evolve due to fluorinated species, landfill bans, biosolid application regulations, and others. A survey of municipalities in the Northeastern United States found that since 2018, sludge management costs have increased by an average of 37% due to polyfluoroalkyl substances (PFAS) alone.[2]

The waste streams being explored also present significant air and water quality hazards. Emissions from wastewater treatment operations in the United States total 18.4 Million Metric Ton CO_2 equivalent/year from CH_4 and 26.4 Million Metric Ton CO_2 equivalent/year from N_2O.[3] Other waste streams such as manure or food waste are readily biodegradable and evolve into methane and other greenhouse gases. When these wastes are landfilled, they often evolve to methane before landfill gas capture infrastructure is installed and operated. More than half of the greenhouse gas emissions from landfilled food waste comes from non-collected methane emissions.[4] HTL as a technology presents promise as a means of preventing these streams from being landfilled or from other fates.

Lastly, organic waste processing facilities are disproportionately sited in disadvantaged communities and communities that are already pollution burdened. There are approximately 3.46 million people living within 2 km of the largest wastewater treatment plants (those processing greater than 50 million gallons of water per day). Of this 3.46 million people, 1.79 million identify as a person of color and/or as low income, 686 thousand are below the poverty line, and 2.13 million reside in neighborhoods that are already above the 90th percentile nationwide for diesel particulate emissions risk.[5,6,7] Wastewater treatment plants are a locus for diesel truck transport for sludge transportation and acceptance of other organic wastes for co-processing. Wastewater treatment sludges are also sources of odor, including hydrogen sulfide, mercaptans, amines, and fecal species.[8] When stored, these wastes can also be breeding grounds for infectious disease vectors and pathogens and result in litter in the neighboring communities.[9] In concert, these factors are associated with mental health deterioration, increased anxiety, depression, and sleep disturbances that are attributable to exposure to these compounds and odors.[1]

There is a need to explore how technologies such as HTL affect these and other sustainability indicators in these community settings. This includes system-level environmental assessment to calculate emissions, baselining as well as ongoing monitoring of air and water quality, and quantifying other emissions that are a result of the HTL process. If technologies such as HTL are to be used in communities to ameliorate these impacts, understanding of other sustainability indicators, both positive and negative, is critical.

3.2 Feedstock Availability

Research groups and technology developers have demonstrated that HTL is amenable for a variety of individual feedstocks. These include algae, organic wastes (municipal sludge, food waste, fats/oils/greases, manure), and forestry residues. In the United States, estimated feedstock availability and fuel yields are provided in Table 1.

Table 1. Wet feedstock availability for hydrothermal processing.

Feedstock	Estimated Feedstock Availability (2017), million dry tons	Estimated Feedstock Availability (2030)	Estimated Fuel Yield (2017), million gallons gasoline equiv.	Estimated Fuel Yield (2030), million gallons gasoline equiv.
Algae	–	24 [11]	–	3,600
Forestry Residues	103 [11]	97 [11]	6,700 [14]	6,300
Fats/Oils/Greases	6.1 [12]	6.6	1,500 [12, 13]	1,600
Food Waste	15.3 [12]	16.7	560 [12, 13]	610
Manure	41.0 [12]	44.7	3,900 [12, 13]	4,300
Municipal Sludge	14.8 [12]	16.1	1,700 [12, 13]	1,900

Each of these feedstocks have their own seasonal and geographical availability differences, as well as local factors (e.g., regulations, beneficial uses) that have created existing supply chains. For example, in the European Union, certain countries prohibit disposal of municipal sludge in landfills and further prohibit its use in land applications - this creates a disposal liability for entities that are responsible for these wastes.

3.3 Feedstock Quality

In the context of the workshop, many participants noted that feedstock quality has critical implications on downstream processing. The composition varies drastically based on the feedstock. Table 2 lists the proximate and the ultimate analysis of some of the different feedstocks available for HTL.

The workshop identified the following key attributes regarding feedstock quality:

- Inorganic content (e.g., Na, K, Fe, Si): presence of mineral species is known to cause catalyst deactivation or plugging during hydroprocessing steps. Some of these mineral species can also have catalytic effects resulting in cracking reactions that affect fuel cuts.
- Nitrogen content: nitrogen-containing heteroatoms are difficult or impossible to separate from the rest of the biocrude once formed. Their presence requires more severe and operationally intensive hydroprocessing steps and could preclude biocrudes from these feedstocks from being accepted (in a co-processing scenario) until their levels are managed.
- Biochemical speciation: the content of fats, proteins, and carbohydrates can provide valuable insight into the resulting biocrude. High-fat and high-lipid feedstocks such as algae or brown grease produce biocrudes that are enriched in diesel-range molecules. Speciation

can also provide insight into the breakdown of n- vs. branched paraffinic content, which has implications for cold flow properties of the resulting fuels.

- Aromatics content: participants noted that higher aromatic content results in biocrudes that contain higher fuel cuts in the kerosene and jet ranges. These aromatic compounds are also required at a certain percent to assure fuel density and to meet the needs of the fuel systems to enable proper sealing.
- Solids content: HTL is typically operated at 20–30 wt % solids content. Higher or lower solids concentration can either require addition of water or dewatering, both of which can have economic and sustainability implications. This also affects rheology and the pumpability of these feedstocks into the HTL reactor.

Table 2. Chemical composition of different HTL feedstocks.

% Feedstock	ULTIMATE ANALYSIS					PROXIMATE ANALYSIS		
	Carbon	Oxygen	Nitrogen	Hydrogen	Sulfur	Fats/Lipids	Carbohydrates	Protein
Algae (chlorella)	53.8	30.8	7.2	7.5	0.6	23.7	23.7	38.6
Food Waste	45.8 - 49.3	35.1 - 37.1	3.2 - 3.4	6.3 - 6.5	0.4 - 0.7	19 - 27	40 - 50	21 - 24
Forestry Residues	50.0	43.6	0.2	6.2	0	0		
Macroalgae (kelp)	32.4	37.9	1.6	3.5	1.2	1.1	58.3	9.8
Manure (dairy)	35.4 - 38.8	54.7 - 57.5	1.3 - 2.4	4.7 - 5.1	N/A			
Manure (swine)	41.1	50.1	3.4	5.4	N/A			
Municipal Sludge	43.6 - 47.8	29.0 - 33.6	3.6 - 7.9	6.5	0.5 - 0.7			

3.4 Feedstock Blending

HTL was noted to have a broad application potential and expanded resource base because of its ability to handle blended feedstocks. Many of the preeminent research and industrial groups employing this technology have demonstrated the ability of their process to handle blended feedstocks, and several of the planned demonstration and commercial facilities are being designed to handle blends (e.g., Tofte, Norway; Calgary, Alberta; and Queensland, Australia).

Workshop participants noted several advantages of blending feedstocks:

- Improved economies of scale: many of the feedstocks (e.g., municipal sludge, food waste) are inherently distributed, so aggregation of multiple feedstocks is necessary to improve economies of scale.

- Temporal variability: feedstocks like algae vary seasonally and blending with other feedstocks can minimize turn-down ratios and improve economics.
- Management and mitigation of feedstock variability: For feedstocks with elevated or decreased attributes, blending with other feedstocks can aid in producing biocrudes that are aligned with downstream specifications (e.g., blending of a low-nitrogen feedstock with a high-nitrogen feedstock).

Blending is not without challenges. Use of blends requires additional logistical supply chains and the associated risks therein. It also requires operators to be aware of the operational challenges of the respective feedstocks that result from their own sources of variability. Participants noted that significant research and development is needed to explore aspects of pumpability, preprocessing and formatting, conversion and hydroprocessing performance, and final fuel quality.

3.5 Feedstock Formatting

While HTL has been tested on a variety of feedstocks, feedstock formatting represents a barrier to further adoption given the variable pumpability between feedstocks. Several of the plenary presentations discussed how pushing to higher solids contents (> 20%) is key to improving yields and operational efficiency. However, at those higher solids concentrations, existing pumping equipment may not be suitable. Participants noted that significant research and development is needed to explore aspects of pumpability, rheology, or preprocessing and formatting steps before feeding into the HTL reactor. Key R&D needs and barriers include:

- Pumpability data: parameterized studies to develop pump curves at varying solid rates and blends of feedstocks.
- Rheology studies: fundamental scientific data to understand flow regimes could benefit pump and heat exchanger design. Heat exchanger efficiency is a critical cost and energy intensity driver given the high amount of water present in the feed streams.
- Homogenization and preprocessing development: understanding the extent to which heat transfer, mass transfer, and conversion efficiency are affected by particle size is largely unexplored. Moreover, techno economic and life cycle analysis to compare tradeoffs of adding these unit operations would be valuable.

Figure 1. Summary of research opportunity topics in the feedstock matters and formatting.

3.6 Research Opportunities in Feedstock

- Feedstock blending: there is a need to understand the implications of processing a variety of wet wastes. Feedstock blending has significant potential to increase plant scale and increase biocrude yield through synergistic effects. In addition to wastewater sludge, fats, oil, grease, food waste, and animal manure represent the full spectrum of waste streams available. The technical challenges and opportunities for each stream are as follows:

  - Food waste: understanding this stream is becoming more urgent because of recent landfill bans on organic waste in many municipalities and some states. Food waste is inherently variable in composition and will require testing as a single stream before consideration as a blend. This stream includes food processing waste, supermarket fresh, household food waste, and institutional cafeteria waste. Aggregation could be an issue, but there will be municipal aggregation services in many areas with organic waste bans. Receipt for processing at the WRRF for blending with sludge is favorable in terms of infrastructure because this waste is often already delivered to WRRF for co-digestion in AD units. Testing food waste individually and as a blend will fill a critical data gap.
  - Animal manure: this stream is contributing to ecological harm in many regions, and large animal feeding operations are actively looking for solutions to meet regulatory requirements and operate more sustainably. The volumes of waste are substantial and relatively homogenous. The challenge is the presence of impurities such as straw and dirt. In many feeding operations, water flush systems are used to clean and transport manure to holding pits and lagoons. The additional water dilutes the feedstock below the threshold for HTL, and dewatering or blending with dry biomass near the source will be required to effectively use such manure.

- Feedstock availability: HTL conversion costs are significantly affected by plant size. Increasing total available feedstocks by including additional wastes such as plastics, municipal solid waste, food waste, manure, and plant or wood wastes has the potential to enable significantly increased regional wet waste blending and plant sizes. Characterizing the feedstock variability as well as demonstrating the viability of processing with a blended feedstock will increase the design HTL plant size, thereby reducing HTL biocrude cost.
- Pumping at scale: pumping of concentrated wet wastes (> 20 wt%) creates many challenges, in part due to rheology and non-uniformity issues. At bench and pilot scales, pumping can be quite challenging. While equipment exists that is designed to pump highly viscous material at industrial scales, there is still a need to better understand feedstock variability and rheology to assure that the right equipment and pre-processing (e.g., grinding and formatting) is utilized for sustained operations.

4.0 Hydrothermal Liquefaction Process

HTL is the thermal conversion of solid feedstocks (e.g., biomass, food waste) into liquid, solid, and gaseous products in a reaction medium of hot compressed water. The overall reaction sequence is hydrolysis to produce monomeric units (sugars, peptides, free fatty acids, and lignin fragments) and the reaction of these units to form biocrude and other organic compounds in primary product streams. Selecting process conditions that favor biocrude formation and optimize nutrient recovery require an understanding of the properties of near-critical water.

The properties of water change when conditions are approaching the critical point (T = 374 °C, P = 22 MPa) to support biomass liquefaction. The dielectric constant decreases by nearly 80%, increasing the solubility of nonpolar compounds, assisting hydrolysis and dehydration reactions, and depolymerizing biomass. At the same time, the ionic product concentration increases with increasing temperature at the pressure required to maintain water in a liquid state. Competing free radical reactions may lead to gasification and/or coke formation. Researchers at Aalborg University demonstrated that the ionic product can be maintained in a suitable range at supercritical temperatures if the pressure is sufficiently high (35 MPa).

The yield, quality, and composition of HTL products are related to the feedstock composition and can be influenced by process conditions and catalysts. In general, higher feedstock loadings, fast heating, increasing reaction temperature, and moderate reaction time (10–30 min) lead to higher biocrude yields and a corresponding lower solids yield. Gas generation tends to increase with reaction temperature. Heteroatom removal tends to increase with increasing reaction temperature. Further understanding is needed on the fate of N and S in the HTL reactor to minimize formation of heterocycles. Yields of water-soluble organic compounds can be influenced by temperature and biomass loading. This group of compounds contains low-molecular-weight organic acids, alcohols, and amines that have high solubilities in water as well as oxygenated or nitrogenous organic compounds with higher carbon numbers (> C6) and limited solubility in water. The latter class achieves an equilibrium solubility between the aqueous and biocrude phases. Some discussion of the influence of the feedstock composition on the reaction and final products is given in the following paragraphs.

Lignocellulosic feedstocks are composed of cellulose, hemicellulose, and lignin. The resulting lignocellulosic biocrude is a complex, viscous, and energy-dense liquid containing thousands of compounds. After hydrodeoxygenation, finished fuels retain much of the cyclic and aromatic content of the biocrude, although some aromatics are saturated to become cycloalkanes. The contribution of each fraction to the products can be summarized as follows.

- The hydrolysis of cellulose and hemicellulose leads to poly- and monosaccharide compounds that can further polymerize into char, condense into higher-molecular-weight cyclic and aromatic compounds, or break down into water-soluble organic acids and alcohols. Maintaining a basic pH through the addition of alkali catalysts promotes base-catalyzed retro-aldol condensation reactions and leads to higher biocrude yields.
- Lignin begins to thermally decompose at 200 °C and is more completely hydrolyzed with increasing temperature. Most of the biocrude produced from lignin is derived from the ether-bonded aromatic ring structure and includes methoxy phenols, naphthenes, asphaltenes, and other oxygen-containing aromatic structures. The lignin fragments can re-combine or react with cellulosic intermediates to create additional rings and branches.

For complex, protein-containing biomass such as microalgae, sewage sludge, and food waste, the biocrude is much different than that from lignocellulosic sources. Characteristically, such biocrude is high in nitrogen that is often present in cyclic nitrogen compounds. The major reactions and products for proteins, carbohydrates, and lipids are as follows.

- Proteins are denatured and hydrolyzed to individual peptides that can repolymerize or undergo a cyclodehydration reaction to form stable cyclic compounds. Nitrogen also partitions to the aqueous phase as ammonia from deamination reactions as well as soluble organic compounds. It is in the gas phase as ammonia and in solids as part of the char.
- Carbohydrates in protein-containing biomass can follow similar reaction pathways as cellulosic materials but may also combine with amino acids to form biocrude products via the Maillard reaction.
- Lipids enter as triglycerides, free fatty acids, and also as cellular phospholipids. Under HTL conditions, the glycerol backbone is removed, and most lipids report to the biocrude phase as free fatty acids and do not substantially degrade or interact with the rest of the liquefied biomass. They can be decarboxylated to form hydrocarbons or, in some cases, the carbonyl group can react with nitrogen compounds to form amides.

For all types of biomass, the mineral content (ash) is an inseparable part of the reaction medium and may participate as a catalyst, although this has not been systematically studied or reported. The low dielectric constant of water near the critical point causes precipitation of mineral solids. For example, the multi-valent cations such as Ca^{2+} and Mg^{2+} can precipitate with sulfate and phosphate anions. This provides a processing opportunity to separate solids from the reaction mixture before cooling to reduce the mineral content of the biocrude and facilitate liquid phase separation. Silica compounds are ubiquitous in waste carbon streams and, because of their unique phase and solubility properties, are often present in the biocrude and aqueous fractions in addition to the solid products (e.g., dirt). The total mineral content of the biocrude affects catalytic upgrading and may require targeted pretreatment of the biocrude before upgrading.

4.1 Historical Development and Scale-up

During the crude oil embargo and resulting high prices of the 1970s, interest in alternative fuels surged and resulted in investments in research and process development. During this time, woody biomass liquefaction was developed based on the earlier Bergius process for the liquefaction of coal. Woody biomass was size-reduced, blended into a pumpable slurry with biocrude and process water, and reacted in near-critical, condensed-phase conditions. A large-scale demonstration plant was built and tested in Albany, Oregon, by the Pittsburg Energy Research Center of the U.S. Bureau of Mines from the late 1970s to 1981. To mitigate the high biocrude recycle rates, researchers at Lawrence Berkeley National Laboratory used dilute acid hydrolysis to soften the feedstock and to prepare the wood slurry in water. Although process development was marching forward at a meaningful rate, numerous technical problems and the end of high oil prices led to a reduced focus on liquefaction processes and the abandonment of this plant and a related plant (the Shell hydrothermal upgrading process) after only several hundred hours of time on stream.

None of the early demonstration plants proceeded to full commercial scale. An analysis of these projects in retrospect indicates that the capital cost for high-pressure reactors and securing financing for early-stage technologies were the biggest obstacles to commercialization. Heavy industry must secure sustained capital investment through demonstration and commercialization because each stage of innovation requires significant capital and a long-time horizon. Other challenges noted were inadequate communication and knowledge sharing among stakeholders.

Between the 1980s demonstration plants and the recent resurgence of interest and research activity in HTL in the early 2000s, the main technical advancements were to demonstrate biomass liquefaction without adding a costly reducing gas (CO/H_2) and further developing biomass pretreatment methods to use water or a recycled aqueous phase as the biomass slurry medium. Other biomass sources, including sewage sludge, were tested over this period, and several small demonstrations were launched that ultimately proved to be short-lived and did not achieve commercialization.

4.2 Current State of the Art and Future Strategies

Shortly after another spike in oil prices in 2008 and amid global aspirations for sustainable fuels to address energy security and climate change, interest in HTL was revived. An early success came when whole algae liquefaction led to higher yields and greater economic viability than competing flowsheets with lipid extraction and biochemical conversion. Once the baseline mass and carbon yields to biocrude were widely known, HTL became an established pathway for biomass conversion. Commercial interest grew during the same period, as evidenced by the formation of small companies or the launch of new initiatives among large companies in Europe, North America, India, and Australia. Recent review papers have captured these developments. Currently, the technology readiness, investor interest, and policy support are conducive to commercial demonstration and implementation of the HTL technology.

Most groups operate at near-critical temperatures (300–350 °C) and in the condensed phase (16–22 MPa). Steeper Energy's Hydrofaction^{TM} process operates at supercritical temperatures for enhanced heat transfer and reaction rate but at high pressure (35 MPa) to keep the ionic product high and help suppress radical reactions. The process developed at PNNL includes solids separation at reaction conditions, but several other groups separate solids after the products are depressurized and cooled. There are diverse approaches for treatment and nutrient recovery from the aqueous and solid products. These will be discussed in Section 6.0, after a discussion of biocrude upgrading in Section 5.0.

The most significant advancement of the last decade has been the transition to continuous tubular reactors at bench and pilot scales. Continuous processing significantly decreases future scale-up risks by directly simulating the reactor conditions and types of equipment needed to pump slurries to high pressure, liquefy biomass, reduce temperature, depressurize the reactor, and separate high-quality products. Tubular reactors also allow for process heat integration by using the heated product stream to pre-heat the incoming feed stream, allowing for 70–80% heat recovery and cutting energy input costs to an attractive range. Several groups have estimated the energy return on investment (EROI) for HTL to be between 3 and 4. That is, for every unit of energy required for HTL conversion, 3 to 4 units of energy are recovered in the liquid biocrude. By comparison, common biofuels such as corn ethanol can struggle to achieve an EROI > 1.

Adding homogeneous or heterogeneous catalysts to the HTL reactor has been investigated by several of the workshop participants and continues to be an active research focus area. The HTL reaction medium presents many challenges because catalysts must tolerate acidic and basic compounds, poisons such as sulfur, and substantial physical solids while sustaining activity and not plugging.

- Homogeneous catalysis using alkali salts such as potassium carbonate are commonly practiced, as discussed above. These catalysts are at least partly consumed in the reaction and serve multiple roles in maintaining pH and promoting condensation reactions.
- Heterogeneous catalysis is less studied but has been shown in some cases to provide greater deoxygenation of the biocrude during the HTL reactions and/or to increase biocrude yields. Key considerations for heterogeneous catalysts include whether they can be in a slurry form with the feedstock or in a fixed bed.
    - Slurry catalysts must at some point be recovered from the process for recycling.
    - Fixed-bed catalysts may be limited by the physical stability of the catalyst support under hydrothermal conditions. Carbon supports are superior in this regard, whereas many zeolite or alumina supports would be challenged.

4.3 Research Opportunities in the HTL Process

HTL process to produce biocrude efficiently and economically requires better understanding on the process integration and demonstration at scale. Several areas of opportunity to enable the HTL process include the following.

- Low-cost feedstocks: because HTL is compatible with wet waste resources, the research and commercial focus is shifting to these low-cost inputs to favor an economic model that combines waste disposal with fuel production. To use low-cost feedstocks of varying composition, continued research is needed to understand the relationship of feedstock composition and processing conditions to the intermediate biocrude yield, composition, and final fuel quality after catalytic upgrading. Research should include enhanced modeling such as reactor-scale engineering models, machine learning models, or elementary reaction models as more data becomes available.
- Pilot-scale demonstrations: many of the workshop participants have built and operated pilot-scale HTL facilities. Several more facilities at even greater scale have been planned and fully designed. As additional plants are commissioned and achieve months of continuous operation, participants agreed that the technical risk is decreased across the board.
- Plant scale and modularization: wet waste feedstocks are geographically distributed and will require transportation to a large central HTL facility or modularization of the HTL reactor for deployment at individual feedstock sources. This is an ongoing optimization question.
- Heat integration: moving to a larger scale will allow design and testing of improved product-feed heat exchangers. Process modeling has shown that heat exchangers represent up to 40% of the installed capital cost; thus, cost reduction through better design will have an outsized impact. Data from improved designs at the pilot scale will lower investment risk.

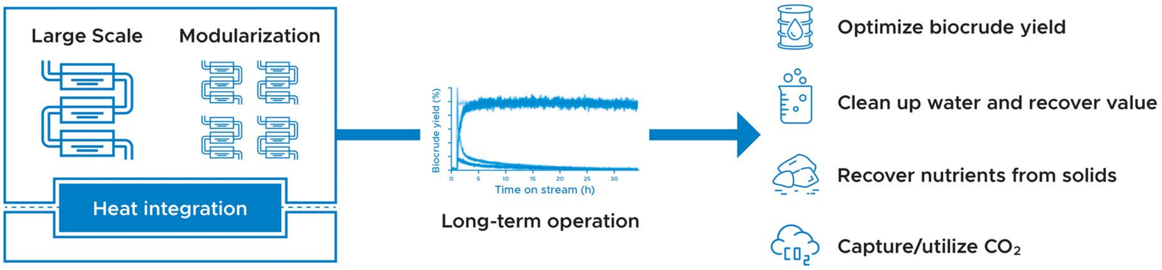

Figure 2. Summary of research opportunity topics in the HTL process.

5.0 Separation and Upgrading

5.1 Hydrothermal Liquefaction Biocrude Upgrading

The most valuable product from the HTL process is the biocrude because it can be upgraded to fuels using standard refinery hydrotreating unit operations designed to upgrade crude oil. Biomass provides hydrocarbon-rich molecules composed of carbohydrates, lignin, proteins, and lipids, all of which are converted to fuel precursors within the biocrude from an HTL process. This biocrude can be burned for heat (e.g., a cement kiln), but producing fuels from HTL biocrude by hydrotreating provides a much-improved value proposition. Hydrodeoxygenation, hydrodenitrogenation (HDN), and hydrodesulfurization can reduce the heteroatom content of biocrudes to produce fuels with less than 0.5% oxygen, 0.25% nitrogen, and < 15 ppm sulfur. The primary challenges to hydrotreating HTL biocrude lie in the differences between HTL biocrude and traditional crude oil. The workshop attendees discussed the differences between HTL biocrudes and traditional crude oil, which will affect the upgrading of the biocrude to a finished fuel or fuel blendstock.

5.2 Biocrude Quality

When comparing HTL biocrudes to pyrolysis oils and traditional crude oils, a few major differences noted by the speakers included increased nitrogen content HTL biocrudes, high metal loadings, thermal stability, and total acid number (TAN). The workshop attendees identified the following critical attributes of HTL biocrudes to produce jet fuel.

- Nitrogen content: Traditional crude oil is 0.1 to 2% nitrogen, and the majority of the nitrogen-containing species goes to vacuum distillation and not to the straight run hydrotreaters to produce straight gasoline, jet, or diesel. HTL biocrudes derived from algae or wet wastes such as sewage sludge, manure, or food waste are high in nitrogen (~6%). As a result, hydrotreating catalysts to remove the nitrogen content will be critical because the current nitrogen spec on jet fuel is quite low.
- Inorganics in the biocrude: Inorganics can plug reactors and poison catalysts, thereby requiring guard beds to extend the main hydrotreater catalyst life. Algae HTL biocrudes tend to be high in Fe (1,000–2,500 ppm) because of their stabilization within porphyrin complexes present in the biocrude. Biocrude from sources other than algae tend to have lower Fe levels (100–300 ppm), but still require hydrodemetallization to remove the iron. Silicon (100s to 1,000s of ppm) crashes out of the biocrude when the water is removed. If not removed before the hydrotreater, Si will deposit at the entrance of the reactor. Salts such as Na, K, and Ca can also be present in the oil in the 100–1,000 ppm range. Complete filtration will also be critical to extend the hydrotreater guard-bed lifetimes.
- The TAN of HTL biocrudes tends to be ~60 mg KOH/g oil. This high TAN is driven by the fatty acid content in HTL biocrude. While the TAN of HTL biocrudes is high compared to traditional crude oils, the high TAN comes from the fatty acids, which are less corrosive than other strong acids found in fuels, such as HCl (organic acids vs. mineral acids). Still, more corrosion studies are needed to obtain a definitive understanding of the implication of HTL biocrude on reactor corrosion.
- The thermal stability of HTL biocrude is high. Several workshop attendees noted that after years of storage of HTL biocrude samples at room temperature, no difference was observed in properties or upgrading performance.

Table 3. Comparison of HTL biocrudes to a traditional petroleum feedstock.[15]

	Pine	Chlorella	Sewage Sludge	Petroleum
Carbon (wt %)	83%	79%	77%	83 - 87%
Hydrogen (wt %)	7%	11%	10%	10 - 14%
Oxygen (wt %)	10%	4%	8%	0.05 - 1.5%
Nitrogen (wt %)	0%	6%	4%	0.1 - 2%
Sulfur (wt %)	0%	1%	1%	0.05 - 6%
H:C (mol ratio)	0.97	1.6	1.57	
HHV (MJ/kg)	35.9	39.6	37.8	
TAN (mg KOH/g oil)	53	53	65	
Density (g/mL)	1.1	0.96	1	
Viscosity (cSt @ 40° C)	> 10,000	295	571	
Moisture (wt %)	17%	12%	13%	
Ash (wt %)	0%	0%	0%	
Filterable Solids (wt %)	0%	0%	0%	

5.3 Upgraded Product Quality

When upgraded, approximately 20% of the produced liquid fuel molecules distill in the jet range (150–250 °C), with approximately 20% being in the gasoline range (ambient temperature to 150 °C), 50% in the heavy diesel range (250–350 °C), and 10% in the heavier-than-diesel range (> 350 °C). The workshop attendees discussed the critical attributes of the hydrotreated jet fuel fraction.

The most challenging hydrotreating requirement for the jet cut is expected to be the final nitrogen content. It is believed the elevated S- and N-containing compounds are produced by reactions between their oligomers. The current nitrogen spec for conventional jet fuel is < 10 ppm (ASTM D1655), in part because traditional jet fuel from a refinery process has very low levels of nitrogen. As a result, it will be important to study the implications of elevated N-containing fuels and their interactions with elevated S-containing fuels, specifically regarding the evolved components (e.g., NOx or thermal stability) from N-rich HTL fuels with and without S-rich traditional jet fuels.

Jet fuel properties from fuels derived from HTL of wet wastes were compared with certified jet fuels. The results indicated that jet fuels derived from biocrude can fit the acceptable distillation range of jet fuel, meet the viscosity (−40°C, −20°C) and density (15 °C and 22 °C) flash point, heat of combustion, and derived cetane number requirements. Still, the properties to monitor include the freeze point arising from the substantial n-alkane content of fuels derived from plant-based lipids contained in many wet wastes. HTL fuels derived from wet waste streams tend to be rich in C16 and C18 n-alkanes due to the fats in the feedstocks; however, these n-alkanes end up in the heavy diesel fraction (250–350 °C) and not in the jet fraction.

5.4 Research Opportunities in Upgrading HTL Biocrude

Upgrading HTL biocrude leverages existing catalyst and process development to also upgrade crude oils. Several areas of opportunity to reduce upgrading costs include the following.

- Improving catalysts to increase the activity in the hydrotreater to achieve an industrially relevant weight hourly space velocity and to reduce the nitrogen content of the upgraded fuel, with catalyst development focused on catalysts specifically for high-nitrogen feedstocks.
- Reducing the guard-bed costs by developing low-cost guard-bed catalysts and possibly non-fixed guard-bed configurations.
- Extending the demonstrated catalyst upgrading experiments to understand catalyst deactivation and establishing commercially relevant catalyst lifetimes.

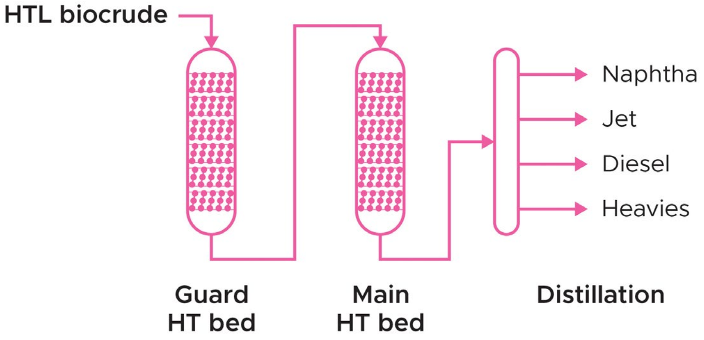

Figure 3. Schematic of the upgrading process for HTL biocrude to fuels.

- Maximizing the value of the heavy fraction through either cracking to increase the jet and diesel yield or producing lubricants.

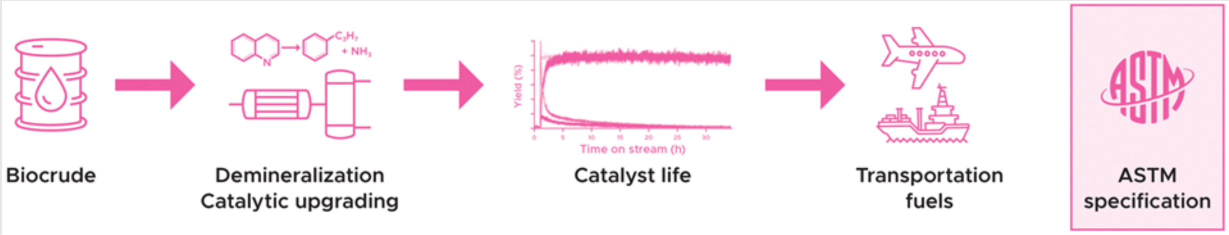

Figure 4. Summary of research opportunity topics in upgrading and refining.

6.0 Other Process Streams

While the biocrude is the most important product from the HTL process, use or treatment of gas, aqueous phase, and solid byproduct streams must be addressed. The gas consists primarily of CO_2, the solids consist of ash and char from the feedstock as well as trapped biocrude, and the aqueous phase consists of a variety of low-molecular-weight components that, at a minimum, must be treated before discharge.

6.1 HTL Solids and Nutrient Recovery

The amount of ash in wet waste streams can vary tremendously, with food and fat streams being low in ash and manures being high in ash. Still, the ash in wet waste streams results in a significant ash byproduct stream. This ash can either be removed at process temperatures and pressures or at ambient conditions. Regardless of the separation strategy, the ash stream is rich in nitrogen and phosphorous and may contain trapped biocrude.

Phosphorus recovery is a clear and current concern for the wastewater community. In the United States, land-applied biosolids can lead to nutrient run-off and ecological harm to surface waters. Over the long term, phosphorus supplies are finite, and recovery of this vital nutrient is not only responsible but may provide nutrient credits to the HTL pathway. HTL may provide a less costly and more effective means of phosphorus recovery and may offer HTL a competitive advantage. Specifically, the vast majority of the phosphorous in wet waste sludges ends up in the HTL ash stream, which could be recycled.

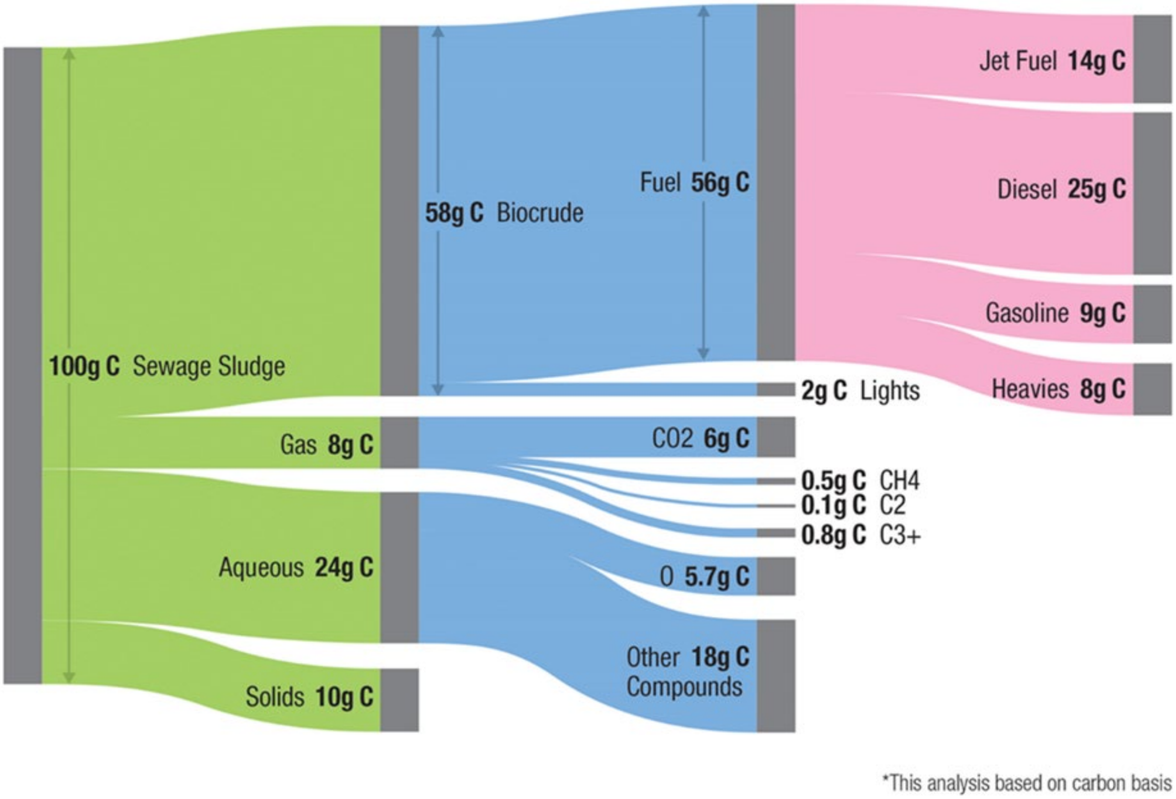

Figure 5. Approximate carbon balance of the ash-free solids content of sewage sludge in an HTL process.

PNNL has estimated that 5 to 10% of the dry, ash-free biomass from HTL ends up in the solids stream, including trapped biocrude due to incomplete separation. This creates an opportunity to further increase the overall biocrude yield via improved solids separation and/or oil recovery from the solids.

Potential applications for the high-ash solid stream depend on the separation efficiency, residual oil content, and phosphorus and nitrogen content. Applications range from use as fertilizer, to disposal at a landfill, to burning at a cement kiln. Additional opportunities include developing new ways to convert nitrogen and phosphorous into forms that can be recovered and used.

6.2 HTL Gas Stream

While the discussion of the HTL gas stream in the workshop was minimal, it is worth noting that the majority of the HTL reactor off-gas is carbon dioxide, followed by hydrogen, methane, and C_{2+} molecules. The overall carbon yield of dry ash-free biomass in a typical low-temperature HTL run to CO_2, CH_4, H_2, C_2 molecules, and C_{3+} molecules is approximately 6%, 0.5%, 0.1%, and 0.8%, respectively. The high CO_2 concentration (> 97%) in the gas stream makes it a high-quality stream for CO_2 upgrading or CO_2 sequestering.

6.3 HTL Aqueous Stream

The HTL aqueous stream was identified as an area of HTL that is both a current liability to the HTL process and an opportunity to improve its value. For dry feedstocks such as woody material, the aqueous stream can be recycled to the headworks of an HTL plant and, in the process, improve the overall biocrude yield. However, recycling the HTL aqueous stream to the headworks of an HTL plant that processes wet wastes such as sewage sludge will dilute the wet waste feedstock and make the process unviable. Sending the HTL aqueous steam to a water resource recovery facility (WRRF) presents challenges by increasing the nitrogen load on the plant, adding toxic components to the feedstock, and potentially hindering the ultraviolet (UV) disinfection process of the treatment facility.

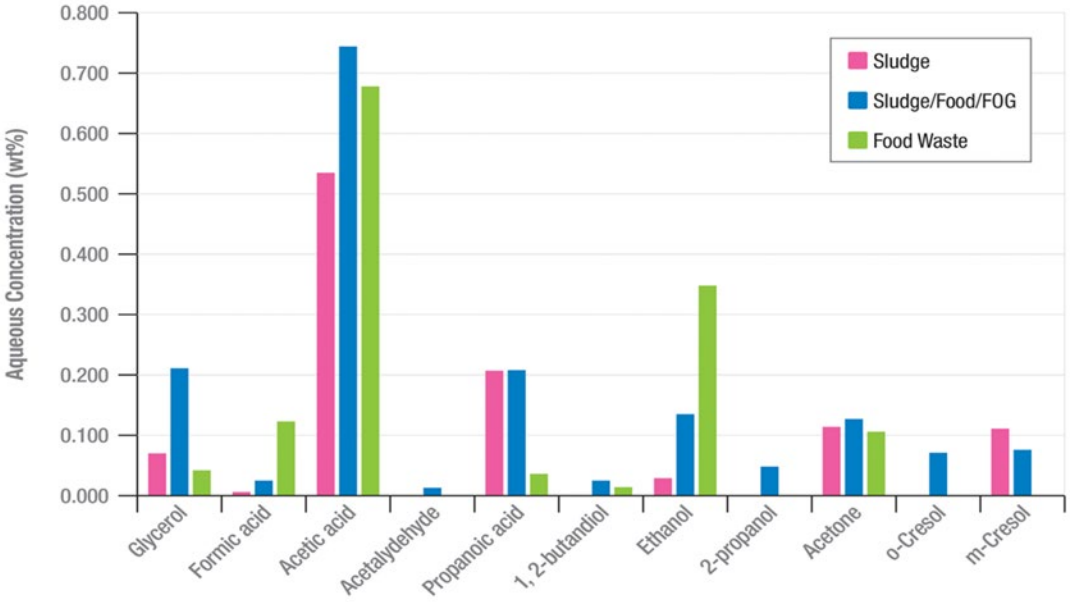

Figure 6. Typical organic composition in the HTL aqueous phase.

As a result, recycling the water was identified as a bigger challenge for wet feedstocks because the feedstock comes in wet, limiting the viability of recycling the aqueous stream. In sub-critical HTL processes, approximately a third of the dry ash-free sewage sludge ends up in the dilute aqueous phase. Part of the challenge in upgrading this stream is that it consists of a mix of many low-molecular-weight and low-value components. Depending on the waste stream, the aqueous product can contain carboxylic acids (mainly acetic acid and propanoic acid), ethanol, acetone, and glycerol. However, the low total organic content (2–3% carbon) in the aqueous stream makes separation challenging. Figure 7 breaks down example aqueous compositions from three continuous HTL experiments with sewage sludge, food waste, and a mix of food waste, sewage sludge, fats, oils, and grease, as determined by liquid chromatography (LC). Additional nitrogen-containing compounds are present that were not identified by LC.

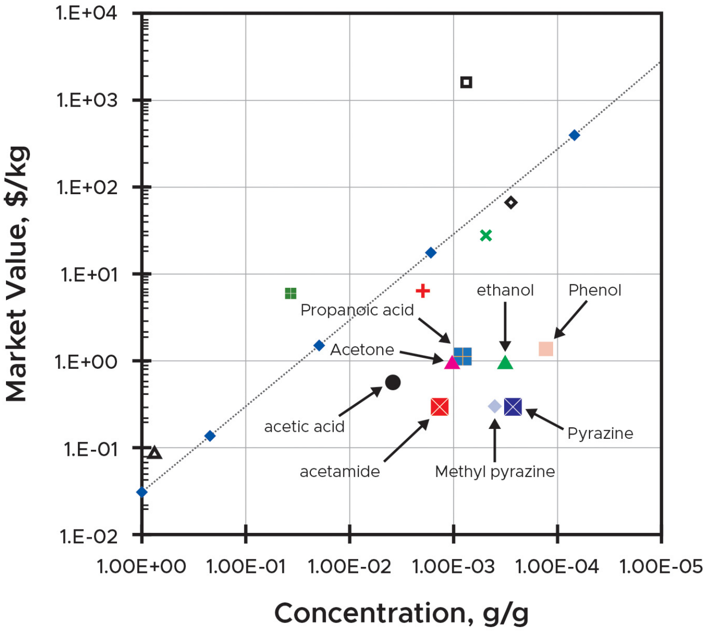

Figure 7. Sherwood plot demonstrating the value of aqueous composition.

A Sherwood plot was shared by one of the presenters that plots the concentration and market value of various components of a typical HTL aqueous stream versus the Sherwood line. The Sherwood line is a quick way to identify if purification of individual components is likely economically viable. The analysis is not favorable for purification of individual chemicals for the aqueous stream. This highlights the need for a low capital, low operational cost conversion or treatment strategy.

The aqueous stream can be a significant liability for an HTL facility depending on the local constraints. If recycled to a wastewater treatment facility, the UV absorbance of the aqueous stream can interfere with UV sanitation, elevated nitrogen levels can push a WRRF beyond their discharge limits, or the components of the aqueous stream can interfere with the facility’s other treatment processes.

6.4 Research Opportunities in Other Process Streams

6.4.1 HTL Aqueous Stream

There is a need to develop a sustainable solution for the HTL aqueous stream, which may include recycling to the headworks of a WRRF. A variety of research efforts are focused on either generating valuable products or fuels or simply cleaning up the aqueous stream from wet waste HTL processes, which cannot recycle the water as easily as HTL processes for dry feedstocks (e.g., wood). Several possible solutions include either conversion or separation of the organics or inorganics from the aqueous stream. The following is a list of several possible separation solutions: (1) resins or other adsorbents to extract phenolics or other compounds; (2) filtration, likely through staged filtration to dewater the aqueous phase or purify various components; (3) purification of N, P, and K for fertilizer applications; (4) stripping of the aqueous stream to purify and remove ammonia; (5) liquid/liquid extraction of the organics from the aqueous phase; (6) gasification; (7) aqueous phase reforming; and (8) electrochemical separation techniques such as electrodeionization. Part of the challenge with separation is (1) the complexity of the HTL aqueous stream, which can plug membranes, filters, resins, or other materials, and (2) the high capital and energy cost of many of these separation techniques.

Another approach being explored is the conversion of the aqueous phase through either biological or thermochemical approaches. Biological routes can both clean up the stream and generate higher-purity products. However, the primary challenge hindering biological conversion of the HTL aqueous phase is the potential inhibitors. Partial oxidation combined with biological conversion has been proposed to be an economically favorable alternative for the treatment of recalcitrant waste streams. Thermochemical techniques are also being developed, such as gasification, that use homogeneous and heterogeneous catalysts to make hydrogen, methane, carbon dioxide, and carbon monoxide. Two keys for an economically viable thermochemical process include (1) reducing catalyst costs by increasing catalyst life, using less expensive catalysts, and increasing catalyst activity, and (2) reducing the costs associated with increased reactor pressure (higher capital costs) and increased temperature (energy costs).

Any aqueous clean-up, upgrading, or purification strategy will need to (1) be low cost, (2) reduce the chemical oxygen demand and the nitrogen content of the aqueous stream, and (3) reduce the UV-Vis absorbance of the aqueous stream.

6.4.2 Solids and Gas

The filtered ash from HTL biocrude can contain a substantial amount of trapped biocrude. This creates an opportunity to further increase the overall biocrude yield via improved solids separation and/or oil recovery from the solids.

The gas from HTL consists primarily of CO_2, making this a promising stream to pair with CO_2 utilization technologies and strategies.

7.0 Call to Action

HTL offers a path to convert wet organic sources, including waste carbon and classical biomass, into fuels that are primarily in the diesel range. Based on the discussions during the workshop, the action items that need to be considered to hasten the commercial deployment of HTL for SAF are listed in the table below.

Table 4. Critical research opportunities and needs in hydrothermal liquefaction technology toward SAFs.

Critical Area	Need	Research Opportunities
Scale-up	Understanding and eliminating the scale-up risk is essiential. The process stability needs to be demonstrated over time in scalable reactor configurations.	• Producing large quantity of finished fuels for fuel stability and engine testing. • Demonstrating HTL process durability for industrially relevant times on stream. • Biocrude upgrading catalyst lifetime for industrially relevant times on stream with stable performance. • Quantifying the feedstock reactor interface constraints at commercially relevant conditions. • Developing models to guide scale-up.
Fuel Quality	Meet stringent fuel quality specifications to achieve aviation industry safety requirements. A concern is the nitrogen content.	• Correlate the feedstock properties and operating conditions with the jet fuel composition (e.g., n-alkane and aromatic composition). • Demonstrate to original equipment manufacturer (OEM) that the fuel can consistently meet the specification irrespective of the feedstock composition. • Understand the interplay between N- and S- content on fuel stability, sooting, and seal swell behavior. • Develop hydrodenitrogenation catalysts for HTL biocrude to sufficiently reduce the nitrogen content below 10 ppm in the jet cut under industrially relevant conditions.
Process Integration	Integrate process steps to reduce the overall capital cost. The primary capital expense is the heat exchangers.	• Understand and address heat and material balance and flows between unit operations. • Identify and demonstrate use or cost-effective treatments for all the product streams (e.g., gas, solid, aqueous, and crude). • Develop back-end processing steps (e.g., cracking) to increase the jet cut (150–250° C) of the distillate above 50%.
Sustainability	Achieve balanced economic, social, and environmental sustainability.	• Understand value along the supply chains (e.g., job creation). • Measure regional needs and plays: cleaning up the ecosystem and environment.

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Appendix A

Workshop Agenda

Day 1 – November 17, 2020, 7:00 A.M. to 11:00 A.M. (PST)

Time	Topic	Speaker
7:00 A.M.	Welcome and workshop objectives	John Holladay, Transportation Sector Lead, PNNL Michael Berube, Deputy Assistant Secretary for Transportation (Acting), U.S. DOE Jud Virden, Associate Laboratory Director, PNNL
7:15 A.M.	Keynote Address	Steve Csonka, Executive Director, CAAFI
7:30 A.M.	Session 1. Current state of hydrothermal liquefaction Session Moderator: Dan Anderson, PNNL	Valentin Batteiger, Bauhaus Luftfahrt Michael Timko, Worcester Polytechnic Institute Paul Kadota, Metro Vancouver Perry Toms, Steeper Energy
7:50 A.M.	Current State of Hydrothermal Liquefaction	Q&A
8:10 A.M.	Break Out: Current state of hydrothermal liquefaction – Feedstock and the fuel production	
8:40 A.M.	Report out	
9:00 A.M.	Break	
9:10 A.M.	Session 2. Fuel quality matters Session Moderator: John Holladay, PNNL	Tim Edwards, Air Force Research Laboratory Josh Heyne, University of Dayton Stephen Lupton, Honeywell UOP Richard Hallen, PNNL
9:30 A.M.	Fuel quality matters	Q&A
9:50 A.M.	Break out: Making the highest quality fuels	

Time	Topic	Speaker
10:20 A.M.	Report out	
10:40 A.M.	Day 1 wrap-up	John Holladay, PNNL, Zia Haq, DOE-BETO

Day 2 – November 18, 2020, 7:00 A.M. to 11:00 A.M. (PST)

Time	Topic	Speaker
7:00 A.M.	Welcome	Manuel Garcia-Perez, Washington State University
7:05 A.M.	Day 1 survey update	John Holladay, PNNL
7:10 A.M.	Session 3. Getting costs down and value up Session Moderator: Carol Sim, Washington State University	Andre Coleman, PNNL Thomas Helmer Pedersen, Aalborg University Mike Thorson, PNNL Michael Wolcott, Washington State University
7:50 A.M.	Getting costs down and value up	Q&A
8:10 A.M.	Break Out: How to get costs down and value up?	
8:30 A.M.	Report out	
8:50 A.M.	Break	
9:00 A.M.	Session 4. Next steps in HTL scale-up and commercialization Session Moderator: Zia Abdullah, National Renewable Energy laboratory	David Chiaramonti, Politecnico di Torino /RE-CORD David Lewis, University of Adelaide Ramesh Bhujade, Independent Consultant Robert Downie, Licella
9:40 A.M.	Next steps in HTL scale-up and commercialization	Q&A
10:00 A.M.	Break out: What are the next steps in HTL scale-up and commercialization?	
10:20 A.M.	Report out	
10:40 A.M.	Day 2 wrap-up	Zia Haq, DOE-BETO Steve Csonka, CAAFI Corinne Drennan, PNNL John Holladay, PNNL

Day 3 – November 19, 2020, 7:00 A.M. to 11:00 A.M. (PST)

Time	Topic	Speaker
7:00 A.M.	Welcome	Corinne Drennan, PNNL Doug Elliott, retired
7:15 A.M.	Session 5. Sustainable Aviation Fuel Certification Session Moderator: Steve Csonka, CAAFI	ASTM Approval process, Mark Rumizen, Federal Aviation Administration Clearing house/ASCENT, Anna Oldani, Federal Aviation Administration CAAFI fuel prescreening, Josh Heyne, University of Dayton
8:10 A.M.	Sustainable Aviation Fuel Certification	Q&A

Time	Topic	Speaker
8:30 A.M.	Break out: HTL needs for ASTM certification, lessons learned, and best practices	
8:50 A.M.	Report out	
9:10 A.M.	Break	
9:30 A.M.	Session 6. Road mapping. Full group discussion for high-level road mapping for hydrothermal liquefaction: paths to sustainable aviation fuel.	John Holladay, PNNL Zia Haq, DOE-BETO
10:40 A.M.	Workshop wrap-up	Karthikeyan Ramasamy, PNNL Zia Haq, DOE-BETO Steve Csonka, CAAFI

Appendix B

Breakout Session Questions

Session 1: Current state of hydrothermal liquefaction process

Day 1: 8:10 A.M.

Moderators: Carol Sim, Derek Vardon, Beau Hoffman, Justin Billing, Mike Thorson, Karthikeyan Ramasamy, Corinne Drennan, John Holladay

1) How does your organization practice HTL?
    - Batch or continuous, what scale, time-on-stream, catalyst (Yes/No), solvent (other than water Yes/No), how do you feed into the reactor, what feedstocks?
    - What experience does your organization have with HTL biocrude upgrading?
    - What experience does your organization have with the aqueous or solid phases?
2) What technical challenges remain for HTL?
    - What scalability challenges remain for HTL?
    - How do we get to 10 million gallons/year or larger?
    - What challenges do we face with HTL byproduct streams (e.g., aqueous phase, ash/char, gas)?
    - How can HTL be used effectively on high-ash feedstocks?
3) What are the advantages and disadvantages of different ways HTL is practiced?

Session 2: Fuel quality matters

Day 1: 9:50 A.M.

Moderators: Carol Sim, Derek Vardon, Beau Hoffman, Justin Billing, Mike Thorson, Karthikeyan Ramasamy, Corinne Drennan, John Holladay

1) What experience does your organization have with producing SAF?
    - How do feedstocks affect the fuel quality?
    - How do processing conditions affect the fuel quality?
    - What is the relative amount of each hydrocarbon fraction (alkanes, branched alkanes, cycloalkanes, and aromatics) relative to your feedstocks?
    - What fraction of the total fuel is SAF?

- What are the challenges of producing reproducible SAF fractions?
- What issues relative to fuel requirements have you found?

2) Would your organization be interested in joining a global 'round table' for studying blend ratios of different feedstocks (e.g., sludge, manure, food waste, forestry residues, agricultural residues, and algae) and other enabling activities? What information can you share now?

Session 3: Getting costs down and value up

Day 2: 7:50 A.M.

Moderators: Carol Sim, Derek Vardon, Beau Hoffman, Justin Billing, Mike Thorson, Karthikeyan Ramasamy, Corinne Drennan, John Holladay

1) What cost-advantaged feedstocks has your organization studied in HTL?
   - What feedstocks are underrepresented, or which need more R&D?
   - What science is missing that could accelerate HTL scale-up?
2) What are the major cost drivers within the framework (e.g., collecting, feeding the reactor, HTL process, conditioning the biocrude, and upgrading the biocrude)?
   - What is your carbon yield and how can it be improved?
   - Where can separation science aid in reducing cost?
   - What are the highest-cost unit operations, and what R&D is needed to reduce the cost of those operations?
   - How do feedstock availability and supply chain affect economics?
   - What are the practical considerations for heat integration and recovery?
3) What is the best use of each stream coming out of the HTL reactor (heavy oil, light oil, aqueous, solids, and gasses)?
4) What are your experiences in determining the value of the social and sustainability aspects of HTL as a means for dealing with waste streams (sludges, manures, etc.), reducing energy, or other considerations?

Session 4: Next steps in HTL scale-up and commercialization

Day 2: 10:10 A.M.

Moderators: Carol Sim, Derek Vardon, Beau Hoffman, Justin Billing, Mike Thorson, Karthikeyan Ramasamy, Corinne Drennan, John Holladay

1) What scale-up activities are ongoing, and what can we learn from them?
2) What are the highest risk unit operations from a scale-up perspective, and what are the research needs?

3) How could government-sponsored research enable scale-up?

4) How do feedstock availability, storage, and transportation affect scale-up?

Session 5: Steps to get fuel ASTM certified – lessons learned

Day 3: 8:20 A.M.

Moderators: Carol Sim, Derek Vardon, Beau Hoffman, Justin Billing, Mike Thorson, Karthikeyan Ramasamy, Corinne Drennan, John Holladay

1) What is your experience with SAF?
    - Have you tested HTL-derived samples for SAF fuel quality?
    - Can you comment on the reproducibility in SAF samples?
    - What do you see as the biggest challenge in making SAF via HTL processes?
2) What is the biggest challenge in bringing SAF to market?
3) What have we not addressed thus far in the workshop sessions that you would like to be considered in an R&D roadmap?

Appendix C

Workshop Panelists

Session 1. Current state of hydrothermal liquefaction, Session Moderator: Dan Anderson, PNNL

Panelist 1: Valentin Batteiger, Bauhaus Luftfahrt

Panelist 2: Michael Timko, Worcester Polytechnic Institute

Panelist 3: Paul Kadota, Metro Vancouver

Panelist 4: Perry Toms, Steeper Energy

Session 2. Fuel quality matters, Session Moderator: John Holladay, PNNL

Panelist 1: Tim Edwards, Air Force Research Laboratory

Panelist 2: Josh Heyne, University of Dayton

Panelist 3: Stephen Lupton, Honeywell UOP

Panelist 4: Richard Hallen, PNNL

Session 3. Getting costs down and value up, Session Moderator: Carol Sim, Washington State University

Panelist 1: Andre Coleman, PNNL

Panelist 2: Thomas Helmer Pedersen, Aalborg University

Panelist 3: Mike Thorson, PNNL

Panelist 4: Michael Wolcott, Washington State University

Session 4. Next steps in HTL scale-up and commercialization. Session Moderator: Zia Abdullah, National Renewable Energy laboratory

Panelist 1: David Chiaramonti, Politecnico di Torino/RE-CORD

Panelist 2: David Lewis, University of Adelaide

Panelist 3: Ramesh Bhujade, Independent Consultant

Panelist 4: Robert Downie, Licella

Session 5. Sustainable aviation fuel certification, Session Moderator: Steve Csonka, CAAFI

Panelist 1: Mark Rumizen, Federal Aviation Administration

Panelist 2: Anna Oldani, Federal Aviation Administration

Panelist 3: Josh Heyne, University of Dayton

Appendix D

Workshop Management Team

Workshop Organizing Team:

Johnathan Holladay (PNNL), Corinne Drennan (PNNL), Karthikeyan K. Ramasamy (PNNL), Asanga Padmaperuma (PNNL), Steve Csonka (CAAFI), Zia Haq (DOE-BETO), Michael Wolcott (WSU), Carol Sim (WSU)

Panel Moderators:

Dan Anderson (PNNL), Johnathan Holladay (PNNL), Carol Sim (WSU), Zia Abdullah (NREL), Steve Csonka (CAAFI)

Panelists:

Valentin Batteiger, (Bauhaus Luftfahrt), Michael Timko (WPI), Paul Kadota (Metro Vancouver), Perry Toms (Steeper Energy), Tim Edwards (Air Force Research Laboratory), Josh Heyne (University of Dayton), Stephen Lupton (Honeywell UOP), Richard Hallen (PNNL), Andre Coleman (PNNL), Thomas Helmer Pedersen (Aalborg University), Mike Thorson (PNNL), Michael Wolcott (WSU), David Chiaramonti (Politecnico di Torino /RE-CORD), David Lewis (University of Adelaide), Ramesh Bhujade (Retired from Reliance, Independent Consultant), Robert Downie (Licella)

Break Out Session Moderators:

Carol Sim (WSU), Derek Vardon (NREL), Beau Hoffman (DOE-BETO), Justin Billing (PNNL), Mike Thorson (PNNL), Karthikeyan Ramasamy (PNNL), Corinne Drennan (PNNL)

Break Out Session Note Takers:

Meshack A. Audu (WPI), Hannah Nguyen (NREL), Jacob Miller (NREL), Stephen Tifft (NREL), Udishnu Sanyal (PNNL), Casper Brady (PNNL), Senthil Subramaniam (PNNL), Mond Guo (PNNL)

Workshop Management:

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